Visible-Light Active Nanomaterials for Environmental Remediation – A Mini Review

Nirupama 1, Badal Kumar Mandal 1,*

1 Trace Elements Speciation Research Laboratory, Department of Chemistry, School of Advanced Sciences, Vellore Institute of Technology (VIT), Vellore - 632014, India
* Correspondence: badalmandal@vit.ac.in (B.K.M.);

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Abstract: For the past few decades, industries like dyeing, paper, and textile industries have been releasing potentially hazardous substances which may affect human health. The majority of the pollutants present in water bodies comprise dyes. Although various traditional methods have been employed to treat wastewater from industries, recent advances in technology depict tapping of solar energy using visible light photocatalysts to remove toxic dyes hazardous to health. Nanomaterials have proved to enhance the properties of any material they are incorporated into, especially due to their increased surface areas in the case of catalysts, resulting in more interaction with the substrate. The uses of nanomaterials in photocatalytic degradation activities have also proven to increase degradation efficiencies. The present study is intended to provide a broad overview of the various contaminants, especially dyes, polluting the environment and the visible-light-active nanomaterials-related technologies available for their degradation. Further, the advantages of using such materials and technologies in improving the environment and human health will be discussed in detail, and the foundation for further development in this area will be highlighted.

Keywords: visible light active nanomaterials; environmental remediation; photocatalyst; photodegradation.

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1. Introduction

Many industries have been releasing potentially hazardous pollutants to the environment for the past few decades, affecting human health [1]. Large volumes and the complex nature of effluents released from textile industries pose a major threat to the environment. It has been observed that dyes form the major component of the pollutants present in water bodies. Dye colors affect the quality of water and hence disrupt the aquatic ecosystem. Due to the carcinogenic, genotoxic, and mutagenic nature of dyes and their partial breakdown resulting products, it causes serious health effects to humans [2]. The conventional methods used to treat water are adsorption, oxidation processes, flocculation, ultrafiltration, etc. But most of these methods do not completely convert the dyes into non-toxic inorganic products like CO2 and H2O, do not have high degradation efficiency, and recyclable and stable photocatalysts.

Several nanomaterials have been used to remove pollutants from the water body and surrounding environment. Especially, silver nanoparticles (Ag NPs) are used extensively as antimicrobial agents [2-6], while other nanomaterials such as silica NPs [7], gold NPs [8], Nano-Sized Zirconium Vanadate [9], titanium dioxide NPs [10], silver vanadate nanorods [11], copper oxide NPs [12], metal sequestration [13], copper NPs [14], zinc oxide NPs [15], nickel
oxide NPs [16], and iron oxide NPs [17] are used pollutant remediation as well as water purification.

However, photocatalysis using solar energy can be used as a clean and cost-effective detoxification technology, using renewable and abundant energy to oxidize organic and inorganic compounds present in contaminated water to a non-toxic form [18-20]. Recently, semiconductor photocatalysts have been widely used for pollutant degradation. Free oxidizing species like hydroxyl and peroxide radicals, electrons, and holes are generated upon irradiation by light in the UV-visible region. Such materials should have the ability to efficiently separate generated electron-hole pairs and reduce their recombination rate for effective dye degradation [21]. The use of nanomaterials has widely increased in recent studies as they have proved to improve the properties of materials when incorporated in them with a higher turnover and efficiency rate. Moreover, nanomaterials play an important role in environmental remediation. It has been used to remove contaminants of size less than 300 nm from water bodies and less than 20 nm from the air [22].

The present study highlights the various visible-light active photocatalysts used for the degradation of dye pollutants. It discusses comparative degradation efficiencies and reaction rates of various photocatalysts.

2. Available nanomaterials for photocatalytic degradation

In this review article, few relevant papers published in ACS since 2012 are reviewed to study various nanomaterials used for photocatalytic degradation of toxic dyes. Black carbon (BC) soot is a globally generated pollutant with various negative effects on humans and the environment. Due to its high adsorption efficiency nanocarbons are derived from it and used for water filtration to remove organic dyes from contaminated water in a single step. Since graphene is one of the most important allotropes of carbon with high surface activities, graphene nanosheets (GNS) were isolated from the soot of waste petrol. Water-soluble graphene nanosheets (wsGNS) were synthesized by simple oxidation of soot using nitric acid and carboxylic acid groups were incorporated onto the surface, which is responsible for creating more active sites on the surface. High-density surface defects due to negative functional groups were confirmed by TEM, HRTEM, and XPS analyses. The wsGNS exhibit photoluminescent properties due to proton transfer between the carboxylate anion/hydroxyl and hydroxyl/hydroxyl moieties, which can be easily tuned by changing the degree of surface functionalization. The high-density surface defects increase the spatial separation between HOMO and LUMO, trap photoexcited electrons during visible light irradiation and generate oxygen radicals on the surface which are responsible for an efficient methylene blue (MB) dye degradation. Hydroxyl radicals also contribute to the degradation process. 96 % of MB was degraded in 90 min by wsGNS, and its rate constant was 0.0313 min⁻¹ compared to GNS, which degraded only 19.6 % of MB with a rate constant of 0.0028 min⁻¹ (~11 times lower). Post-degradation studies of MB confirmed the destruction of the aromatic structure of the dye that resulted in smaller hydrocarbons as the degraded products. The degradation efficiency reduced to 90 % after 3 cycles and 75 % after 5 cycles of photocatalyst recycling. The synthesis of a highly stable, recoverable, and reusable photocatalyst derived from pollutant soot using a low-cost, facile, metallic contamination-free method is the advantage of this process [20].

A conducting polymer polyaniline/reduced graphene oxide (PANI/RGO) photocatalyst with sheet-like composites showed excellent degradation activity to rhodamine B (RhB) and malachite green (MG) cationic dyes and congo red (CR) anionic dye when compared to
individual PANI or RGO photocatalysts. RGO helps prevent agglomeration of PANI nanoparticles which enhances the surface area, acts as an electron acceptor, and helps in increasing charge separation, thereby improving light absorption capability. The composite can absorb in the wavelength range of the entire solar spectrum, separating excited charge carriers rapidly, preventing electron-hole recombination, and reducing toxic Cr(VI). The decrease in the bandgap, firm attachment of RGO to PANI, and other structural details were confirmed by various spectral analyses like TEM, FESEM, XRD, and UV-vis spectra. BET analysis indicates a mesoporous structure of the sample with a surface area of 35.06 m$^2$/g. The PANI/RGO composite with 5 wt% RGO showed the highest degradation efficiency (99.68%) for MG dye within 15 min followed by 99.35% RhB and 98.73% CR dyes within 30 and 40 min, when compared to individual PANI (61.07, 70.46, and 73.66%) and RGO (91.54, 89.45, and 86.07%) degraded MG, RhB, and CR dyes, respectively [23]. The rate constants of the PANI/RGO composite for MG, RhB, and CR degradations are 3.84×10$^{-1}$, 0.168, and 0.109 min$^{-1}$, respectively. The photocatalytic activity was mainly found to be due to hydroxyl radicals and partly due to superoxide radicals and holes (h$^+$). The composite showed high photostability even after 6 cycles with degradation efficiencies of 99.68–86.63% for MG, 99.35–87.12% for RhB and 98.73–92.78% for CR. It also efficiently removed 94.7 % Cr(VI) at pH 2 in just 15 minutes [23].

A highly permeable mesoporous Cu$_{1.94}$S-rGO composite was synthesized by hydrothermal method as a photocatalyst for dye degradation and a modified Cu$_{1.94}$S-rGO/GCE phenol sensor which showed a good response toward phenol in 0.2µM to 1.4 µM concentration range. Due to the smaller bandgap of the composite and lesser concentration of photogenerated radicals, the wet hydrogen peroxide catalytic oxidation method (WHPCO) is employed, resulting in high efficiency and low discharge of secondary pollutants in air and water. Attaching RGO to copper monosulphide enhanced electronic mobility. The photocatalyst's mesoporous nature with higher surface area leads to better adsorption of dye molecules and light energy. The successful synthesis of Cu$_{1.94}$S-rGO and GO sheets was confirmed by SEM and TEM analyses. It also confirms the self-aggregation of Cu$_{1.94}$S to form corresponding nanoclusters, which are not evenly distributed on the GO sheet surface, proof for electrostatic interaction due to carboxyl groups on the surface of GO sheets. The average atomic ratio (%) of Cu and S was found to be 1.932:1. XRD confirms the reduction of GO into RGO and the djurleite structure of synthesized nanoparticles, whereas EPR analysis confirms the +1 oxidation state of Cu in Cu$_2$-S and Cu$_2$-S-rGO. The BET analysis revealed a surface area of 16.12 m$^2$/g for Cu$_{1.94}$S and 109.95 m$^2$/g for Cu$_{1.94}$S-rGO. The average pore radius was ~2.98 nm for Cu$_{1.94}$S-rGO and 39.25 nm for Cu$_{1.94}$S calculated using the Barret-Joyner-Halenda (BJH) method. It was observed that the carbon framework disintegrates due to the removal of groups containing oxygen when the temperature rises from 250-800°C. The composite shows enhanced absorption in the near-infrared region (NIR). The photodegradation rate of methyl orange (MO) dye is 0.0019 min$^{-1}$, and Crystal Violet is 0.0022 min$^{-1}$ for Cu$_{1.94}$S-rGO, whereas for Cu$_{1.94}$S, the rates are 0.0007 min$^{-1}$ and 0.0010 min$^{-1}$, respectively. The degradation rate also increases with an increase in the concentration of hydrogen peroxide. Moreover, dye removal efficiency is higher in the case of anionic crystal violet dye than MO as the photocatalyst has negatively charged hydroxyl groups on its surface. The π-π interaction between crystal violet and the localized π orbitals of conjugated aromatic rings of r-GO sheets increases its adsorption to the surface of the photocatalyst. Hence, the degradation efficiency for Crystal violet is 90.76% with 0.55 mM HP dose and 79.44% RE with 0.55 mM HP dose for MO dye. Recycling
the photocatalyst 4 times led to removal efficiency loss of only ~6.8 % for Crystal violet and ~5.1 % for MO [24].

Ag@SnO2-g-C3N4 nanostructures with spherical Ag nanoparticles were biogenically synthesized using a microorganism containing electroactive biofilm as a green, reducing tool for photocatalytic degradation of dye molecules such as MB, CR and RhB. The degradation efficiency of 6 mM Ag@SnO2-g-C3N4 with a high number of Ag nanoparticles was ~99.4 % for MB, ~98.28 % for CR, and ~94.67 % for RhB, and the degradation completed in 90, 60, and 240 minutes, respectively. The degradation rate was highest for 6 mM Ag@SnO2-g-C3N4 compared to 1 mM and 3 mM Ag@SnO2-g-C3N4 nanoparticles. Attaching Ag nanoparticles to SnO2-g-C3N4 lowered the electron-hole pair recombination rate and increased visible light photocatalytic degradation due to surface plasmon resonance. The photocatalyst is responsible for high electron mobility. Stability studies proved that there was no leaching of individual metals due to sonication. Hence the photocatalyst is highly stable. XRD analysis proved the purity and tetragonal rutile structure of SnO2. It also showed that the introduction of Ag improved the crystallinity of the material.

FT-IR spectra proved the presence of hydroxyl groups on the catalyst's surface responsible for the photocatalytic activity and proved the absence of any chemical bonding between Ag nanoparticles and SnO2-g-C3N4. Increased absorbance of the photocatalyst in the visible light region was proved by UV analysis, and PL analysis indicated that loading more Ag on the nanoparticle could lead to better performance. TEM analysis indicated the presence of small, spherical SnO2 nanoparticles (~3 nm) uniformly distributed over g-C3N4. HRTEM confirmed the crystalline nature of SnO2-g-C3N4 nanosheets. Photoelectrochemical studies of FTO-modified Ag@SnO2-g-C3N4 nanostructures showed that combining SnO2 onto g-C3N4 improved recombination lifetime by forming a heterojunction that effectively separates electron-hole pair. Moreover, EIS analysis proves lower charge transfer resistance of the FTO-modified Ag@SnO2-g-C3N4 nanostructures. The rate constants for the degradation of MB, CR, and RhB with 6 mM Ag@SnO2-g-C3N4 nanoparticles were found to be 0.051, 0.059, and 0.009 min⁻¹, respectively, and the reactive oxygen species responsible for the photocatalytic degradation are 'OH and 'O₂⁻ [25].

Degradation studies of RhB were carried out using heterostructures of CdS/NaTaO3 in the presence of visible light. The photocatalyst was prepared initially by surface functionalizing bare NaTaO3 using 3-mercaptopropionic acid, followed by fabrication of various concentrations of CdS. The average particle size of NaTaO3 is 100 nm with a cube shape and synthesized by hydrothermal method. The heterojunction is responsible for decreased electron-hole pair recombination and hence enhanced photocatalytic activity. Raman spectroscopy and PXRD analysis indicated the existence of NaTaO3 in both monoclinic and orthorhombic phases. FESEM, TEM and HRTEM analysis of NaTaO3 nanocubes with uniform spherical 10 nm-sized CdS nanoparticles on its surface retained the shape of NaTaO3 but making the surface rough. BET analysis indicated that incorporation of CdS nanoparticles resulted in increased surface area and pore size making the material mesoporous. The optimum concentration is CdS molar ratio of 8 in Cd/Ta heterostructures. The degradation efficiency of the photocatalyst for RhB is 97.2 % and the degradation time is 110 minutes, and the rate constant of the reaction is 0.327 min⁻¹. After recycling for 3 times, the degradation efficiency was found to be 93.2 %. High crystallinity, expanded visible-light absorption, high surface area, and efficient photogenerated charge carrier separation are few factors that result in a potential photocatalyst for efficient dye degradation [26].
Four different orthorhombic nanomaterials of iron-(oxalate) capped Fe, Cu, Co, and Mn-doped heterobimetallic oxide were synthesized by a redox reaction between [Fe(ox)−Fe(0)] and CuSO₄, CoNO₃, and KMnO₄ in water for dye degradation of MB and other dyes into CO₂, NO₃⁻, and SO₄²⁻. Holes and hydroxyl radicals are majorly responsible for the photocatalytic activity of the nanomaterial. It was observed that protonated MB undergoes faster degradation than neutral MB in acidic pH due to its increased adsorption to the negatively charged catalyst’s surface. The nanomaterials also showed degradation of phenol and the rate of degradation decreases in the order: UV > yellow LED > visible light and Fe(ox)Fe-MnOₓ > Fe(ox)-FeO₄ > Fe(ox)FeCoOₓ > Fe(ox)Fe-CuOₓ with photocatalysts for both phenol and dyes. XRD analysis confirmed amorphous nature of Fe(ox)Fe-MnOₓ and orthorhombic form of Fe(ox)-FeO₄, Fe(ox)Fe-CuOₓ and Fe(ox)Fe-CoOₓ, whereas HR-SEM images confirmed nanoribbon-like structures for Fe(ox)-Fe₃O₄, particle-like nature for Fe(ox)Fe-MnOₓ and orthorhombic morphology for Fe(ox)Fe-CuOₓ and Fe(ox)Fe-CoOₓ. HRTEM analysis indicated porous morphology for Fe(ox)Fe-CoOₓ and Fe(ox)Fe-MnOₓ. The rate constant for Fe(ox)Fe-MnOₓ in the presence of visible light is $17 \times 10^{-3}$ for MB and $12.1 \times 10^{-4}$ min⁻¹ for phenol. The nanomaterial can be used to degrade dyes like methylene blue (MB), malachite green (MG), crystal violet (CV), and methyl violet (MV). However, they show no photocatalytic activity towards dyes like rose Bengal, methyl orange, methyl red, and congo red due to the lack of binding of neutral and anionic dyes to the negatively charged photocatalyst. It is also observed that Fe(ox)Fe-CoOₓ exhibited the most efficient degradation even after 10 cycles, whereas the other nanomaterials exhibited significant efficiency loss and leaching of metals. For large-scale photocatalytic degradation, although the best efficiency was exhibited by Fe(ox)Fe-MnOₓ Fe(ox)Fe-CoOₓ proved to be the most stable nanomaterial [27].

Degradation of RhB using Keplerate {Mo₇²Fe₃₀} nanoclusters was studied. Due to greater surface area, higher pore volume, and negative surface charges amorphous form of Keplerate is considered superior to its rhombohedral crystalline form. Electron transfer from excited polyoxometalates (POM), which produced RhB⁺ and reduced POM (POM⁻) is predicted as a probable mechanism for photocatalytic degradation. The photocatalyst exhibits 100 % degradation efficiency in 1 hour. However, in large-scale degradation, efficiency slightly reduces to 87 % in 4 hours. The optimum pH to be maintained is 2.5, and the optimum dosage of catalyst is 3 mg in 50 mL RhB solution. Although both anionic and cationic dyes undergo degradation, efficiency is lower for anionic dyes like MO. The catalyst was stable for 5 cycles [28].

Titanium dioxide (TiO₂) decorated elongated rhombic shape silver chromate (Ag₂CrO₄) was coupled with gold (Au) and reduced graphene oxide by impregnation and in situ reduction with acacia gum, a reducing and stabilizing agent, to prepare a biogenic photocatalyst and study the degradation of MB dye. The photocatalyst exhibited a degradation efficiency of 97% in 52 minutes with a rate constant of 0.0566 min⁻¹ and a high electron movement capacity. Incorporation of Au and r-GO reduced band vitality increased light ingestion of quaternary Ag₂CrO₄/TiO₂/Au/r-GO composite biofilm photocatalyst and decreased the rate of electron-hole pair recombination. Decoration of TiO₂, an electron sink, on Ag₂CrO₄ also plays a major role in delaying the recombination process. The degradation rate of the newly synthesized film was 10.8, 6.5, and 3.1 times faster than Ag₂CrO₄, Ag₂CrO₄/TiO₂, and Ag₂CrO₄/TiO₂/Au biofilms, each. FESEM analysis confirms 30-40 nm particle size of TiO₂ nanoparticles, and XRD confirms orthorhombic Ag₂CrO₄, anatase TiO₂, and fcc structure of Au. Degradation activity was mainly carried out due to the formation of active hydroxyl radicals and minorly
due to the valence bond holes. The photocatalyst showed excellent stability with a degradation efficiency of 91% after 5 cycles [29].

A magnetically recoverable NiFe$\text{Fe}_2\text{O}_4$/2D MoS$_2$-Pd nanocomposite was synthesized to degrade RhB dye using the hydrothermal method. NiFe$\text{Fe}_2\text{O}_4$/2D MoS$_2$ p-n heterojunction was formed by the interfacial contact between NiFe$\text{Fe}_2\text{O}_4$ nanocubes and corrugated MoS$_2$ nanosheets with Pd nanoparticles distributed uniformly on the surface, and it has improved light absorption efficiency. Here, Pd nanoparticles act as an electron reservoir and lead to localized surface plasmon resonance (LSPR), MoS$_2$ has a large surface area, high thermal stability with greater adsorption ability towards RhB dye, and NiFe$\text{Fe}_2\text{O}_4$ gives good magnetic separability and catalytic recyclability and thereby together enhance the photocatalytic dye degradation process. SEM and TEM images indicated curled paper-like morphology for MoS$_2$ nanosheets without any stacking. In situ formation of Pd nanoparticles and NiFe$\text{Fe}_2\text{O}_4$ nanocubes that homogeneously intercalate into MoS$_2$ layers prevent restacking of MoS$_2$ nanosheets. They also indicate the uniform distribution of Pd nanoparticles over the surface. Pd nanoparticles have an average diameter of 4 nm. The hybrid photocatalyst showed a degradation efficiency of 95.3% for RhB in 30 minutes compared to 59.2% for a physical mixture of NiFe$\text{Fe}_2\text{O}_4$ + 2D MoS$_2$-Pd. Superoxide and hydroxyl radicals play a major role in photocatalytic degradation. The photocatalyst exhibited stability up to 3 cycles with no significant loss of activity [30].

Reduced graphene oxide (rGO) decorated with neodymium, nitrogen, and sulfur tridoped titania (Nd, N, S-TiO$_2$) was used to check photocatalytic degradation of erichrome black T (EBT) and eosin blue shade (EBS) in sunlight and was compared with the degradation activity of corresponding MWCNTs. The degradation was carried out in both single and mixed dye solutions, and degradation of 99.3% was observed in the case of EBS and 94.6% in the case of EBT in single dye solution and 65.7% and 58.9%, respectively, a mixed dye solution. The degradation values are higher than that of commercial and tridoped titania. The rate constant for EBS degradation was found to be 1.4 x 10$^{-2}$ and 1.9 x 10$^{-2}$ min$^{-1}$ for MWCNT/Nd,N,S-TiO$_2$, and rGO/Nd,N,N,S-TiO$_2$, respectively. On the other hand, for EBT the values were 8.0 x 10$^{-3}$ and 1.1 x 10$^{-2}$ min$^{-1}$ for MWCNT/Nd,N,S-TiO$_2$, and rGO/Nd,N,S-TiO$_2$, respectively. Superoxide and hydroxyl radicals are the active species responsible for photocatalytic degradation. Carbon nanomaterials like CNTs and rGOSs help improve optical and photocatalytic properties compared to pure titania by increasing the surface area of the catalyst, adsorption capacity for pollutants, and decreasing titania nanoparticles’ aggregation. TEM and FE-SEM analyses suggest full coverage of reduced graphene sheets by titania nanoparticles. Unlike MWCNTs, there is more interaction between graphene sheets and tridoped titania, leading to better light absorption of the formation of sub-bandgap states in the titania bandgap. XRD patterns suggest the crystalline nature of photocatalyst with the anatase phase of titania. Peaks due to Nd$_2$O$_3$ are absent, which indicates its small amount compared to titania and that it has been well dispersed within the titania matrix. The surface areas of rGO/Nd,N,S-TiO$_2$ and MWCNT/Nd,N,S-TiO$_2$ are 144.87 and 128.21 m$^2$/g, respectively, which is higher compared to tridoped titania with a surface area of 78.21 m$^2$/g. TOC values of 82.0% and 75.6% were obtained for EBS and EBT, indicating fairly high degradation of both the dyes. Nd$^{3+}$ helps increase charge separation and rGOSs and MWCNTs in increasing surface area and preventing aggregation of titania nanoparticles. As a result, they contribute towards enhancing the photocatalytic activity of the catalyst [18].

Gold nanoparticle-mixed metal oxide nanocomposites were synthesized by self-assembly, dihydrolipoic acid (DHLA)-capped gold nanoparticle solution, and mixed metal
oxide (MMO) nanoplates were prepared. The synthesized photocatalyst was then tested for degradation activity against Orange II azo dye under visible light. The DHLA-capped gold nanoparticle had an average diameter of 3.6 nm, a hydrodynamic diameter of 4.7 nm, and was pseudospherical in shape. The MMO nanoplates had hexagonal shapes and a lateral dimension of 100-250 nm. The mechanism followed in this process is as follows: under visible light irradiation, the dye molecule gets excited and transfers the electrons to the semiconductor photocatalyst’s conduction band, which is trapped by the oxygen molecules adsorbed on its surface. As a result, reactive oxidation species are generated that eventually results in either self-degradation of the dye or degradation due to the reactive oxidation species. 99.9999 % of the dye degraded in 2 hours' time, and the photocatalyst could be efficiently reused up to 5 cycles. Au NPs acting as electron sink is the major highlight of this method, which helps efficient visible-light photocatalysis [31].

Ag nanotubes were synthesized from copper nanowires, and by reaction with FeCl₃ hollow plasmonic Ag@AgCl nanotubes were obtained. The degradation of MO was studied, and it was observed that the photocatalyst showed a degradation efficiency of 92.58 %, and the dye degraded in just 10 minutes. The tubulate structure of the photocatalyst provides a larger surface, including the inner and outer surface areas, and acts as a trap-well for photons, which increases light absorption and improves photocatalytic activity. SEM and TEM images indicate the diameter of the photocatalyst to be 0.5-1.5 μm. The rough and porous surface of the catalyst also helps in enhancing the absorption of the dye. Although Ag nanotube is silk-grey in color, Ag@AgCl nanotube is purple. The absorption range increases from 350-800 nm in the case of Ag@AgCl nanotube compared to 200-350 nm in the case of Ag nanotubes. It was observed that the highest photocatalytic activity was obtained when Fe and Ag were mixed in 1:1 ratio. Cl³⁻ and superoxide radicals are responsible for degradation, and the recyclability of the catalyst is 4. The catalyst showed similar results for degradation of RhB as well, and degradation efficiency of 88 % was observed for phenol [32].

AgBr/Ag₃PO₄ decorated ceria nanoflake composites were used for photocatalytic degradation of methylene blue and Methyl orange (anionic and cationic dyes) under visible light. It also showed antimicrobial activity, which was demonstrated with the help of E.coli bacteria. Silver semiconductors help in reducing the rate of electron-hole pair recombination, which enhances photocatalytic activity. Silver ions are also well known for their antibacterial activity. XRD analysis indicates fcc structure for AgBr and Ag₃PO₄. Ceria usually absorbs in the UV region. However, coupling it with AgBr and Ag₃PO₄ shifts the absorbance visible light region due to the presence of Ce³⁺. SEM analysis proves the flake structure of ceria in the synthesized photocatalyst. When combined with AgBr and Ag₃PO₄, the surface areas of the photocatalyst are 92 and 76 m²/g, which are lower than pristine and PEG-assisted ceria. TEM analysis indicated that the size of ceria nanoflakes was between 100 and 200 nm. XPS analysis shows the presence of both Ce³⁺ and Ce⁴⁺ and Ag in the ground state. AgBr/Ag₃PO₄/ceria composite exhibited maximum degradation, whereas the least activity was exhibited by AgBr/ceria composite. The rate constant of AgBr/Ag₃PO₄/ceria composite for degradation of Methylene blue is 577 ± 4.3 x 10⁻⁴ min⁻¹ and for Methyl orange is 339 ± 3.3 x 10⁻⁴ min⁻¹. It also shows antimicrobial activity against E.coli with a rate constant of 206.8 ± 2.9 x 10⁻⁴ min⁻¹. Bacterial activity is caused due to the formation of hydroxyl and superoxide radicals and hydrogen peroxide. On the other hand, dye degradation was mainly caused due to holes followed by hydroxyl and superoxide radicals. The catalyst could be reused 7 times [33].
Electrochemically active biofilms supported on carbon paper were used to synthesize Au@CeO₂ nanocomposites in water at 30 degrees Celsius and normal pressure. Hence, fossil fuel needs to maintain reaction conditions, use of harmful chemicals, capping, and reducing agents could be eliminated. The optical and visible light photocatalytic activity was mainly enhanced due to the interfaces present between Au NPs and CeO₂. MO and MB were used to analyze the degradation activity. Au NPs help CeO₂ absorb light in the visible region. PL spectrum revealed fluorescence quenching from CeO₂ by Au NPs due to strong anchoring of Au nanoparticles and, as a result, reduces electron-hole recombination rate. SEM and TEM analysis revealed mostly cube-shaped CeO₂, although some were diamond and triangular in shape and their sizes ranged from 20 to 30 nm. HAADF-STEM image suggests a polycrystalline structure for Au@CeO₂ nanocomposites where 2 phases had fcc lattices. Au NPs had a size ranging from 6-10 nm, were evenly distributed over CeO₂ surface, and did not undergo self-aggregation. XPS analysis proved Ce⁴⁺ state of CeO₂ and the ground state of gold NPs. The degradation efficiency for MO is 80 % in 6 hours, and MB is 95 % in 5 hours. Superoxide and hydroxyl radicals are responsible for the degradation process. The catalyst could be reused 3 times which reduces degradation efficiency only to 90 % [34].

Ag₂S-grafted NiO–ZnO ternary nanocomposites were synthesized by precipitation method and used for visible-light photocatalytic degradation against RhB with a degradation efficiency equal to 95 % in 120 minutes. The best activity was exhibited by 8 % Ag₂S/NiO–ZnO (AZN-8), and the species responsible for degradation activity are superoxide and hydroxyl radicals. A rate constant of 0.0302 min⁻¹ was observed for the degradation of the dye molecule. Surface plasmon resonance of silver plays a major role in enhancing the photocatalytic activity of the nanomaterial. XRD analysis proved the hexagonal shape of ZnO and fcc structure of NiO. TEM analysis predicted the spherical shape of NiO particles. The randomly scattered Ag₂S NPs on NiO– ZnO surface create irregularities and contribute to better photocatalytic activity. The photocatalyst retained a degradation efficiency of 85 % after 6 recycles. The photocatalyst also has the ability to detect acetone with a sensitivity of 4.0764 μA mmol L⁻¹ cm⁻² and a lower detection limit equal to 0.06 mmol L⁻¹ [35].

3. Discussion

Various research articles based on visible-light active nanomaterials for dye degradation were reviewed. Nanomaterials such as wsGNS, PANI/RGO, Cu₁.₉₄S-rGO, Ag@SnO₂-g-C₃N₄, CdS/NaTaO₃, Fe(ox)Fe-MnOₓ, Fe(ox)Fe-CoOₓ, Mo₇₂Fe₃₀, Ag₃CrO₄/TiO₂/Au/r-GO, NiFe₂O₄/2D MoS₂-Pd, rGO/Nd,N,S-TiO₂, Au NP-MMO, Ag@AgCl, AgBr/Ag₃PO₄/ceria, Au@CeO₂, and Ag₂S/NiO–ZnO were used to study the degradation of dyes such as MB, MG, RhB, CR, MO, Crystal violet, EBS, EBT, and Orange II. Among the research articles reviewed, 6 catalysts were used for degradation of RhB dye, 6 for MB, 4 for MO, 2 for CR, and 1 each for other dyes. PANI/RGO could degrade MG, RhB, and CR, Ag@SnO₂-g-C₃N₄ could degrade MB, CR, and RhB, Cu₁.₉₄S-rGO could degrade MO and Crystal violet, Au@CeO₂, and AgBr/Ag₃PO₄/ceria could degrade both MO and MB and rGO/Nd,N,S-TiO₂ could degrade EBS and EBT.

The catalysts used for the degradation of RhB are PANI/RGO, AZN-8, Ag@SnO₂-g-C₃N₄, CdS/NaTaO₃, Mo₇₂Fe₃₀, and NiFe₂O₄/2D MoS₂-Pd. The highest degradation efficiency (100 %) is exhibited by Mo₇₂Fe₃₀, whereas the highest no of recycles (n = 6) was possible using PANI/RGO with a recycling efficiency of 87.12 %. For MB, the highest degradation efficiency of 99.4 % was exhibited by Ag@SnO₂-g-C₃N₄, whereas the highest...
number of recycles was possible using AgBr/Ag<sub>3</sub>PO<sub>4</sub>/ceria nanomaterial. In the case of MO, maximum degradation efficiency (92.58 %) and the maximum number of recycles were obtained using Ag@AgCl nanotubes. Both photocatalysts PANI/RGO and Ag@SnO<sub>2</sub>-g-C<sub>3</sub>N<sub>4</sub> used to degrade CR dye showed almost equal degradation efficiencies of 98.73 and 98.28 %. However, with PANI/RGO the time required to degrade was lesser (40 minutes) compared to that required by Ag@SnO<sub>2</sub>-g-C<sub>3</sub>N<sub>4</sub> (60 minutes), and the rate constant is also higher for PANI/RGO (0.109 min<sup>-1</sup>) with not much loss in efficiency after 6 recycles. Hence PANI/RGO would be a better visible-light active photocatalyst for CR.

The advantage of using wsGNS photocatalyst to degrade MB dye is that it is a highly stable, recoverable, and reusable photocatalyst derived from pollutant soot using a low-cost, facile, metallic contamination-free method. PANI/RGO is a nanocomposite capable of absorbing the entire portion of the solar spectrum. It also efficiently removes Cr(VI) up to 94.7% at pH 2 in only 15 minutes. Cu<sub>1.94</sub>S-rGO nanomaterial, along with degradation of MO dye and Crystal violet, also shows a good response toward phenol in 0.2µM to 1.4 µM concentration range. But it was observed that the carbon framework disintegrates due to the removal of oxygen-containing groups when the temperature rises from 250-800°C, and the wet hydrogen peroxide catalytic oxidation (WHPCO) method is required for enhanced photocatalytic degradation. More the concentration of hydrogen peroxide greater the number of hydroxyl radicals generated for photodegradation and reduces electron-hole pair recombination. The advantage of using NiFe<sub>2</sub>O<sub>4</sub>/2D MoS<sub>2</sub>-Pd photocatalyst is that it is a magnetically recoverable catalyst. And can be used as a catalyst for the Suzuki-Miyaura coupling reaction. On the other hand, AgBr/Ag<sub>3</sub>PO<sub>4</sub>/ceria nanomaterial showcases antimicrobial property along with dye degradation. Ag@AgCl nanomaterial exhibits similar degradation efficiency for RhB as MO and also degrades phenol by 88%. A green method was adopted to synthesize Au@CeO<sub>2</sub> to degrade MO and MB, without burning fossil fuels and avoiding the use of toxic chemicals. AZN photocatalyst also has the ability to detect acetone with high sensitivity, and it degrades RhB by 95%.

Meanwhile, orthorhombic iron-(oxalate) capped Fe, Cu, Co, and Mn-doped heterobimetallic oxide nanomaterials exhibit the highest photocatalytic activity in the presence of UV light and least in the presence of visible light. Moreover, they show no photocatalytic activity towards dyes like rose Bengal, methyl orange, methyl red, and congo red due to lack of binding of neutral and anionic dyes to the negatively charged photocatalyst. Similarly, Keplerate {Mo<sub>72</sub>Fe<sub>30</sub>} does not degrade anionic dyes efficiently, and with an increase in pH of the medium above 5, photocatalytic efficiency decreases. But it shows 87% degradation efficiency towards RhB in large-scale degradation.

4. Conclusions

Although many toxic dyes are released into water bodies by various industries every year without proper treatment, various scientific methods have been identified to treat contaminated water. The use of visible-light active nanomaterials has been the recent advanced, cost-effective technology preferred by many scientists to degrade such harmful dyes to simpler and less harmful compounds like CO<sub>2</sub> and H<sub>2</sub>O. Few relevant research articles published in ACS since 2012 were reviewed to study various visible-light active nanomaterials available for dye degradation. Among the photocatalysts used to degrade Rhodium B dye highest efficiency was exhibited by Mo<sub>72</sub>Fe<sub>30</sub>, whereas PANI/RGO along with degradation of RhB could degrade Malachite green, Congo red dyes as well as Cr (VI) and could be reused in 6 cycles.
methylene blue best efficiency was exhibited by Ag@SnO$_2$-g-C$_3$N$_4$, and in the case of methyl orange, it was Ag@AgCl nanotubes. However, for CR degradation PANI/RGO is a better photocatalyst than Ag@SnO$_2$-g-C$_3$N$_4$.

Table 1. Performance summary of visible-light active nanomaterials for dye degradation.

<table>
<thead>
<tr>
<th>Photocatalyst</th>
<th>Dye</th>
<th>Degradation efficiency (%)</th>
<th>Time (min)</th>
<th>Rate constant (k/min$^{-1}$)</th>
<th>No. of recycles</th>
<th>Recycling efficiency (%)</th>
<th>ref</th>
</tr>
</thead>
<tbody>
<tr>
<td>wsGNS</td>
<td>MB</td>
<td>96</td>
<td>90</td>
<td>0.0313</td>
<td>3</td>
<td>90</td>
<td>75</td>
</tr>
<tr>
<td>PANI/RGO</td>
<td>MG</td>
<td>99.68</td>
<td>15</td>
<td>0.384</td>
<td>6</td>
<td>86.63</td>
<td>34</td>
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<tr>
<td></td>
<td>RhB</td>
<td>99.35</td>
<td>30</td>
<td>0.168</td>
<td></td>
<td>87.12</td>
<td></td>
</tr>
<tr>
<td></td>
<td>CR</td>
<td>98.73</td>
<td>40</td>
<td>0.109</td>
<td></td>
<td>92.78</td>
<td></td>
</tr>
<tr>
<td>Cu$_{18}$S-rGO</td>
<td>MO</td>
<td>79.44</td>
<td></td>
<td>0.0019</td>
<td>4</td>
<td>74.34</td>
<td>35</td>
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<td></td>
<td>Crystal violet</td>
<td>90.76</td>
<td></td>
<td>0.0022</td>
<td></td>
<td>83.96</td>
<td></td>
</tr>
<tr>
<td>Ag@SnO$_2$-g-C$_3$N$_4$</td>
<td>MB</td>
<td>99.4</td>
<td>90</td>
<td>0.051</td>
<td>-</td>
<td>-</td>
<td>36</td>
</tr>
<tr>
<td></td>
<td>CR</td>
<td>98.28</td>
<td>60</td>
<td>0.059</td>
<td>-</td>
<td>-</td>
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<tr>
<td></td>
<td>RhB</td>
<td>94.67</td>
<td>240</td>
<td>0.009</td>
<td>-</td>
<td>-</td>
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<tr>
<td>CdS/NaTaO$_3$</td>
<td>RhB</td>
<td>97.2</td>
<td>110</td>
<td>0.327</td>
<td>3</td>
<td>93.2</td>
<td>37</td>
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<tr>
<td>Fe(ox)Fe-MnO$_x$</td>
<td>MB</td>
<td>-</td>
<td>-</td>
<td>0.017</td>
<td>4</td>
<td>-</td>
<td>38</td>
</tr>
<tr>
<td>Fe(ox)Fe-CoO$_x$</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>10</td>
<td>-</td>
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</tr>
<tr>
<td>Mo$<em>7$Fe$</em>{30}$</td>
<td>RhB</td>
<td>100</td>
<td>60</td>
<td>-</td>
<td>5</td>
<td>-</td>
<td>39</td>
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<tr>
<td>Ag$_2$CrO$_4$/TiO$_2$/Au/r-GO</td>
<td>MB</td>
<td>97</td>
<td>52</td>
<td>0.0566</td>
<td>5</td>
<td>91</td>
<td>40</td>
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<tr>
<td>NiFe$_2$O$_4$/2D MoS$_2$-Pd</td>
<td>RhB</td>
<td>95.3</td>
<td>30</td>
<td>-</td>
<td>3</td>
<td>-</td>
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<tr>
<td>rGO/Nd,N,S-TiO$_2$</td>
<td>EBS</td>
<td>99.3</td>
<td>240</td>
<td>-</td>
<td>-</td>
<td>29</td>
<td></td>
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<tr>
<td></td>
<td>EBT</td>
<td>94.6</td>
<td>240</td>
<td>-</td>
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<tr>
<td>Au NP-MMO</td>
<td>Orange II</td>
<td>99.9999</td>
<td>120</td>
<td>-</td>
<td>5</td>
<td>-</td>
<td>42</td>
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<tr>
<td>Ag@AgCl</td>
<td>MO</td>
<td>92.58</td>
<td>10</td>
<td>-</td>
<td>4</td>
<td>-</td>
<td>43</td>
</tr>
<tr>
<td>AgBr/Au+PO$_4$/ceria</td>
<td>MB</td>
<td>-</td>
<td>60</td>
<td>0.0577</td>
<td>7</td>
<td>-</td>
<td>44</td>
</tr>
<tr>
<td></td>
<td>MO</td>
<td>-</td>
<td>60</td>
<td>0.0339</td>
<td>7</td>
<td>-</td>
<td></td>
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<tr>
<td>Au@CeO$_2$</td>
<td>MO</td>
<td>80</td>
<td>360</td>
<td>-</td>
<td>3</td>
<td>90</td>
<td>45</td>
</tr>
<tr>
<td></td>
<td>MB</td>
<td>95</td>
<td>300</td>
<td>-</td>
<td>3</td>
<td>90</td>
<td></td>
</tr>
<tr>
<td>Ag$_2$S/NiO− ZnO (8%) (AZN-8)</td>
<td>RhB</td>
<td>95</td>
<td>120</td>
<td>0.0302</td>
<td>6</td>
<td>85</td>
<td>46</td>
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</table>

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Conflicts of Interest

The authors declare no conflict of interest.

References


